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17 – 20 March, 2015
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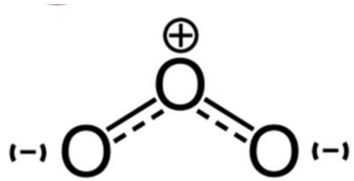
DTU Environment
Department of Environmental Engineering

Ozone chemistry



t½, 20 °C = 3 days

t½, 20 °C = 20 min

Increased pH

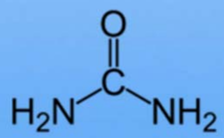
$$O_3 + H_2O \xrightarrow{^-OH} 2\,^{\cdot}OH + O_2$$

Contaminants

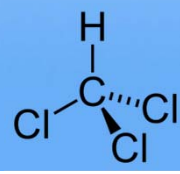
Low reactivity:

$^{\cdot}OH + R \rightarrow R_{ox}$

Urea



Organo-chlorine



High reactivity:

$O_3 + R \rightarrow R_{ox}$

double bond

Ozone chemistry

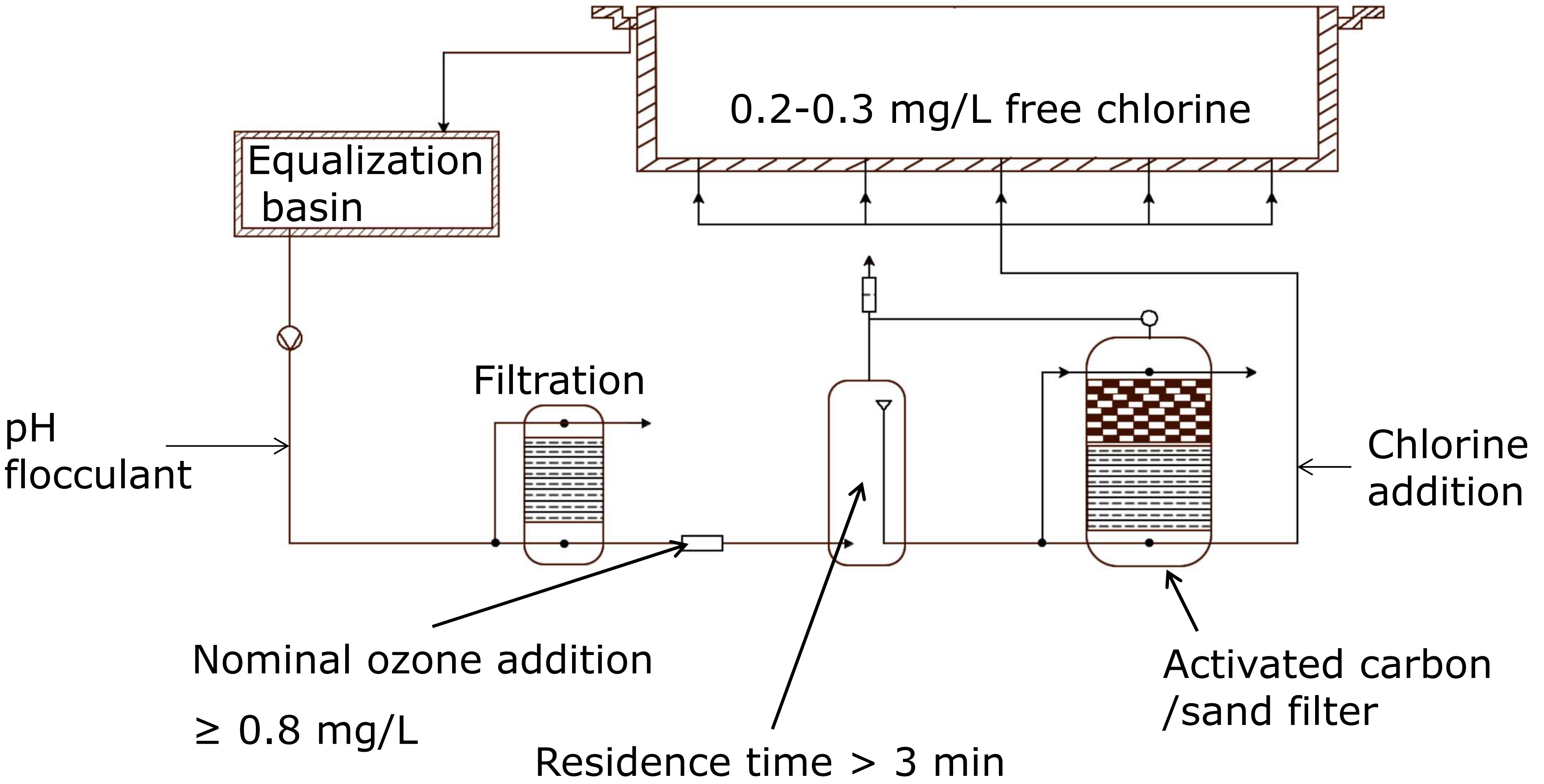
I. Organic matter reactive with ozone

- Direct oxidation by ozone
- Fast consumption of ozone
- Decrease chlorine reactivity of pollutants
- Low ozone life time → no reaction with bromide

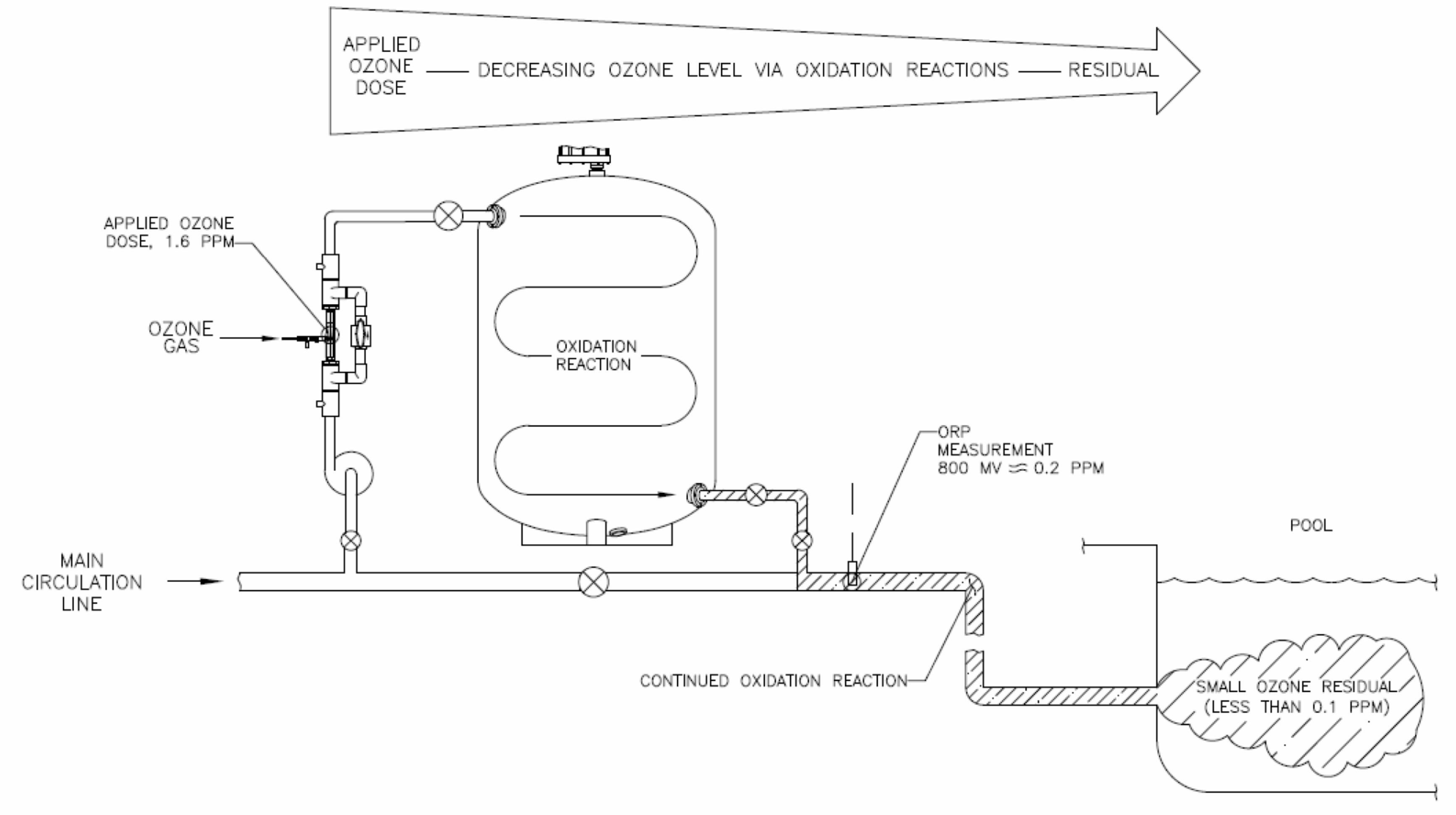
II. Organic matter not reactive with ozone

- Slow consumption of ozone
- Ozone converts to hydroxyl radicals with time
- Radical attack of inactive carbon → increased chlorine reactivity
- Long ozone life time → oxidation of bromide to bromate

Systems: DIN (German standard)



Systems: Slip-stream (USA)



DEL Ozone proprietary drawing

Our aim

Optimizing ozone treatment

- Contact time
- Required ozone dose to minimize chlorination DBPs

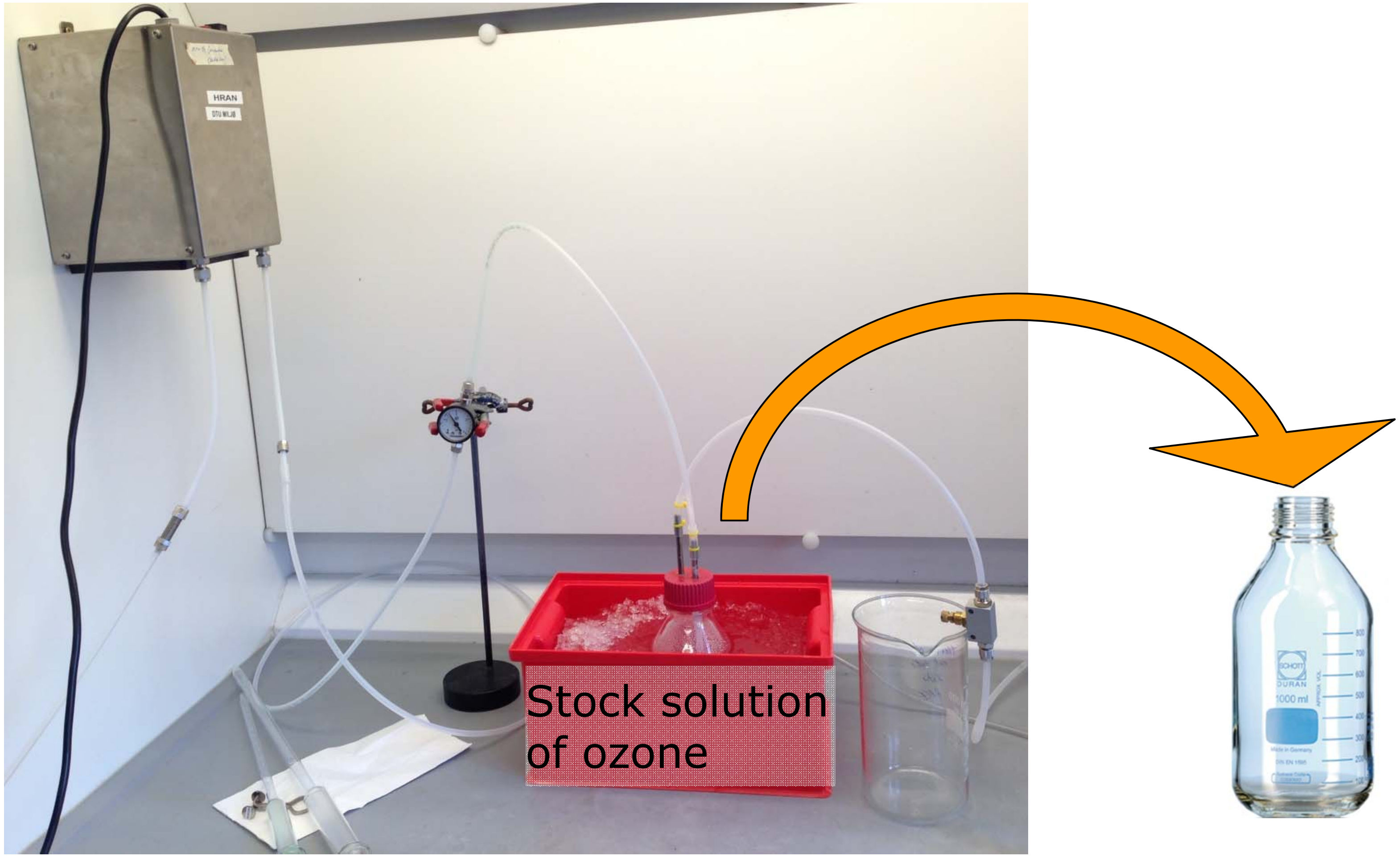
Ozone kinetics not well described in swimming pools

- Effects of pH
- Effects of organic, repeated ozonation

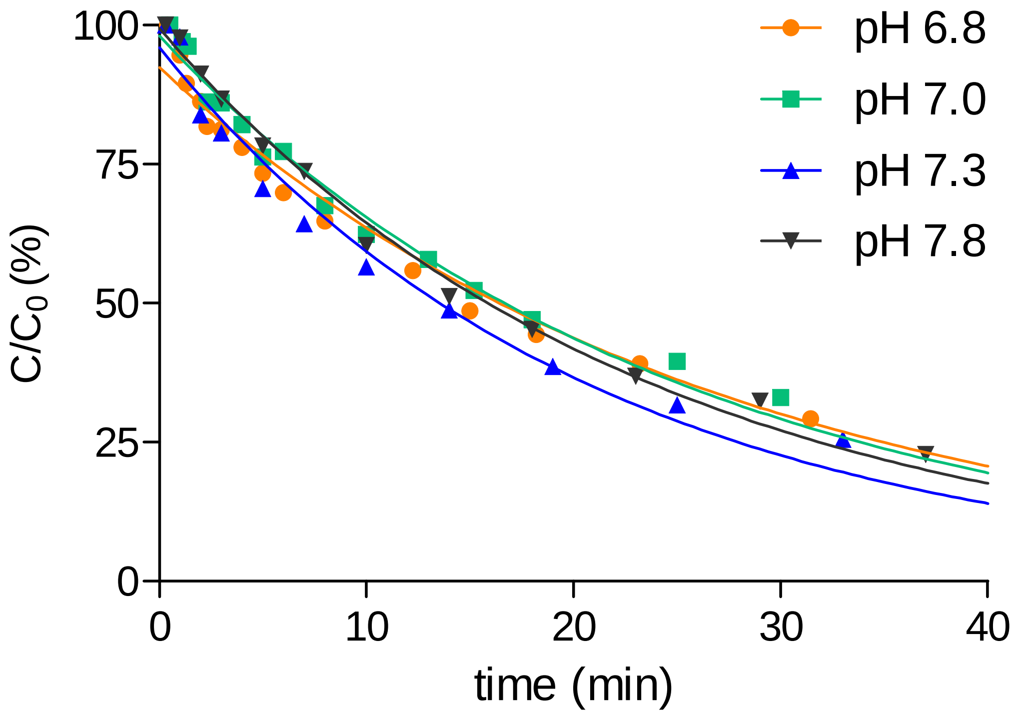
Effect of ozonation on DBP formation

- Pool water
- Filling water
- Fresh pollutants

Lab-scale experiments

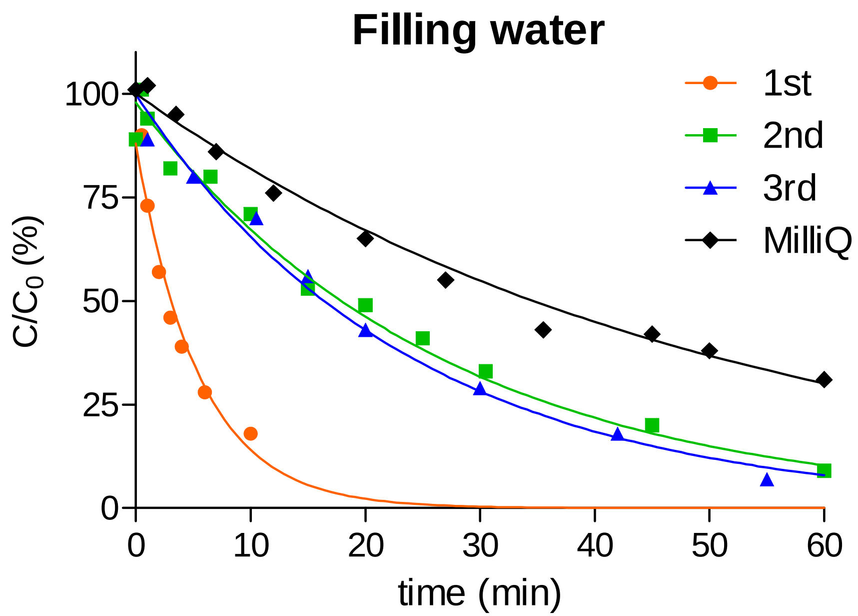


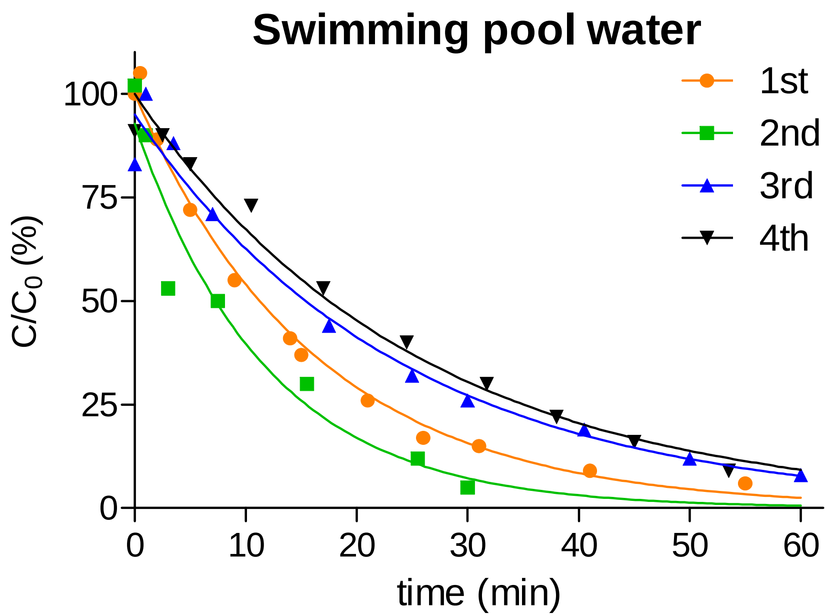
Effect of pH on ozone lifetime



- Very little difference in the pH range swimming pools are operated

Repeated ozonation – ozone lifetime





- Fast removal of 1st ozone dose → ozone reactive material
- 2nd and 3rd → no ozone reactive material

- Little difference → no ozone reactive material in the water

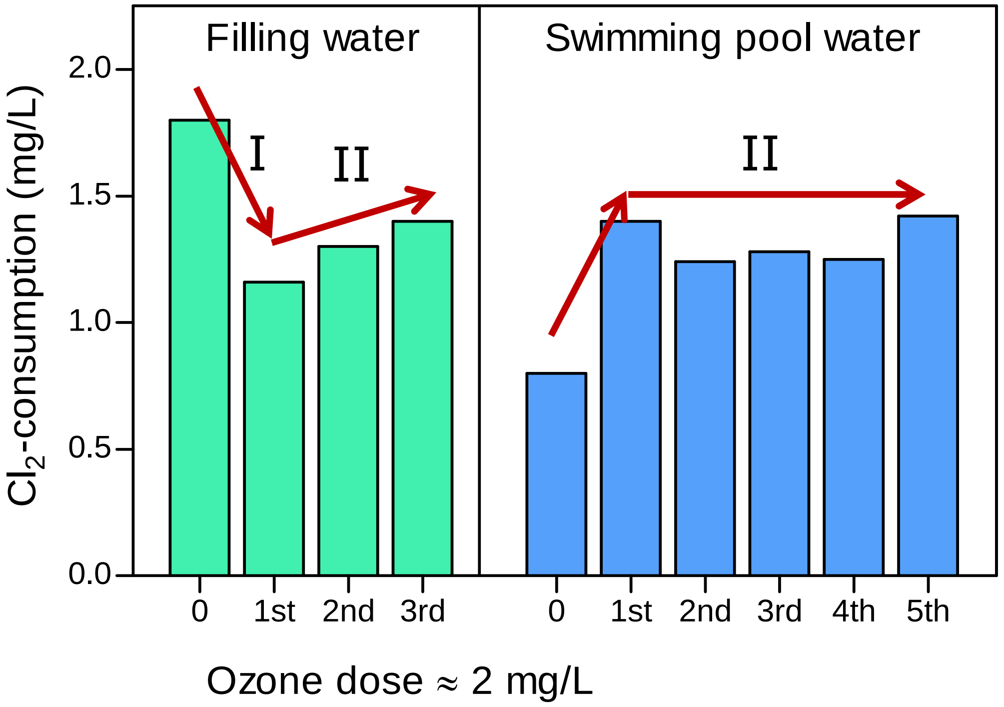
Chlorination of the ozonated samples

Chlorine: 24 h at 25 °C

Chlorine residual +

Purge & trap – GC/MS

Chlorine consumption

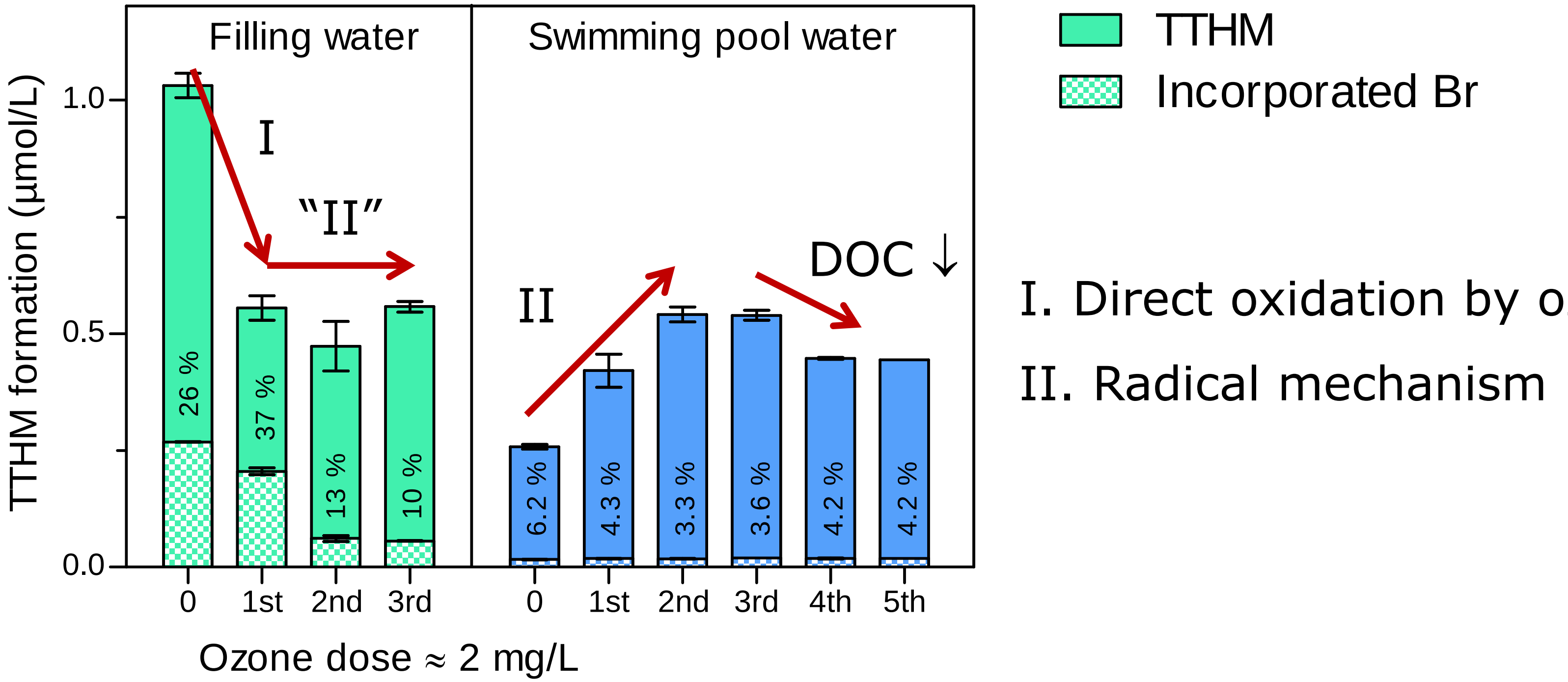


I. Direct oxidation by ozone

II. Radical mechanism

- Different chlorine consumption for tap water and swimming pool water

Formation of total trihalomethane



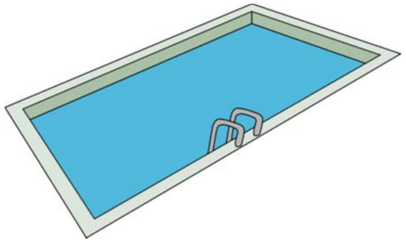
I. Direct oxidation by ozone

II. Radical mechanism

- Ozonation of filling water → decreased THM
- Ozonation of swimming pool water → increased THM

Fresh pollutants

Why do not we see an decrease in THM formation in pool water?



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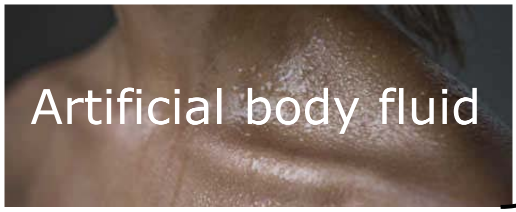
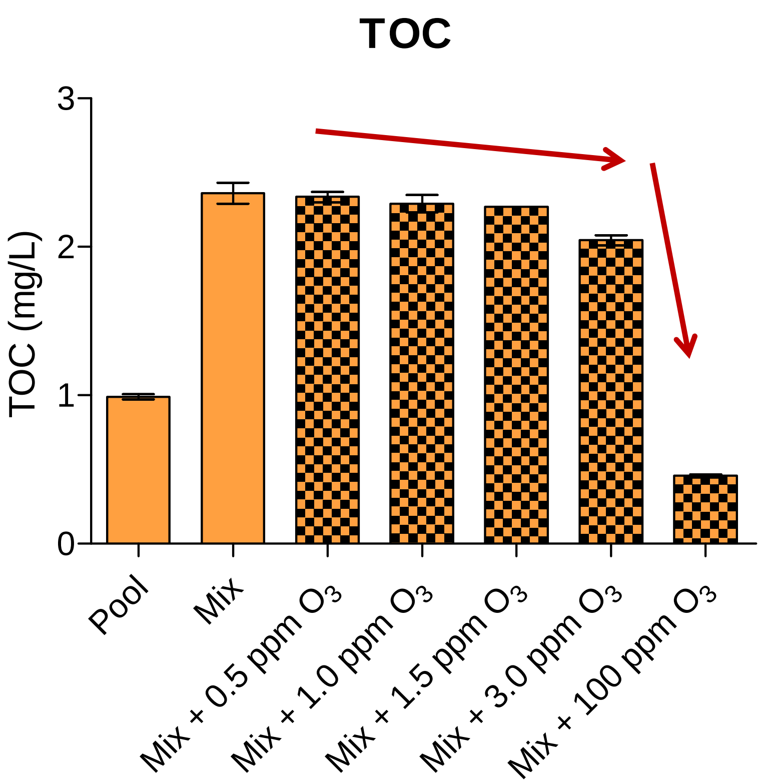
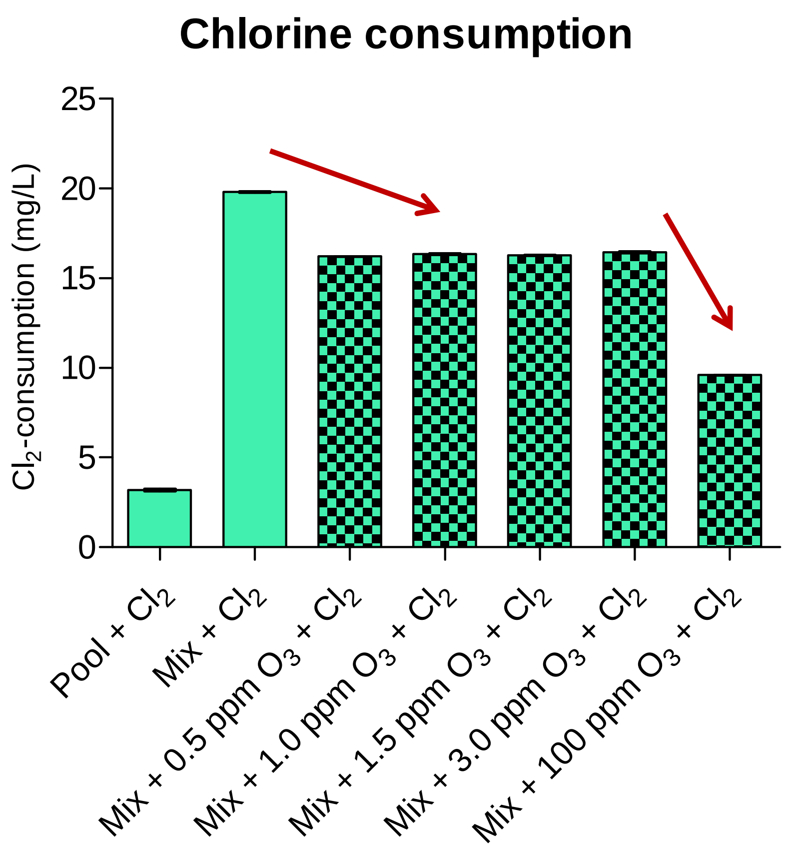


- Control
- 0.5 ppm O_3
- 1.0 ppm
- 1.5 ppm
- 3.0 ppm
- +100 ppm

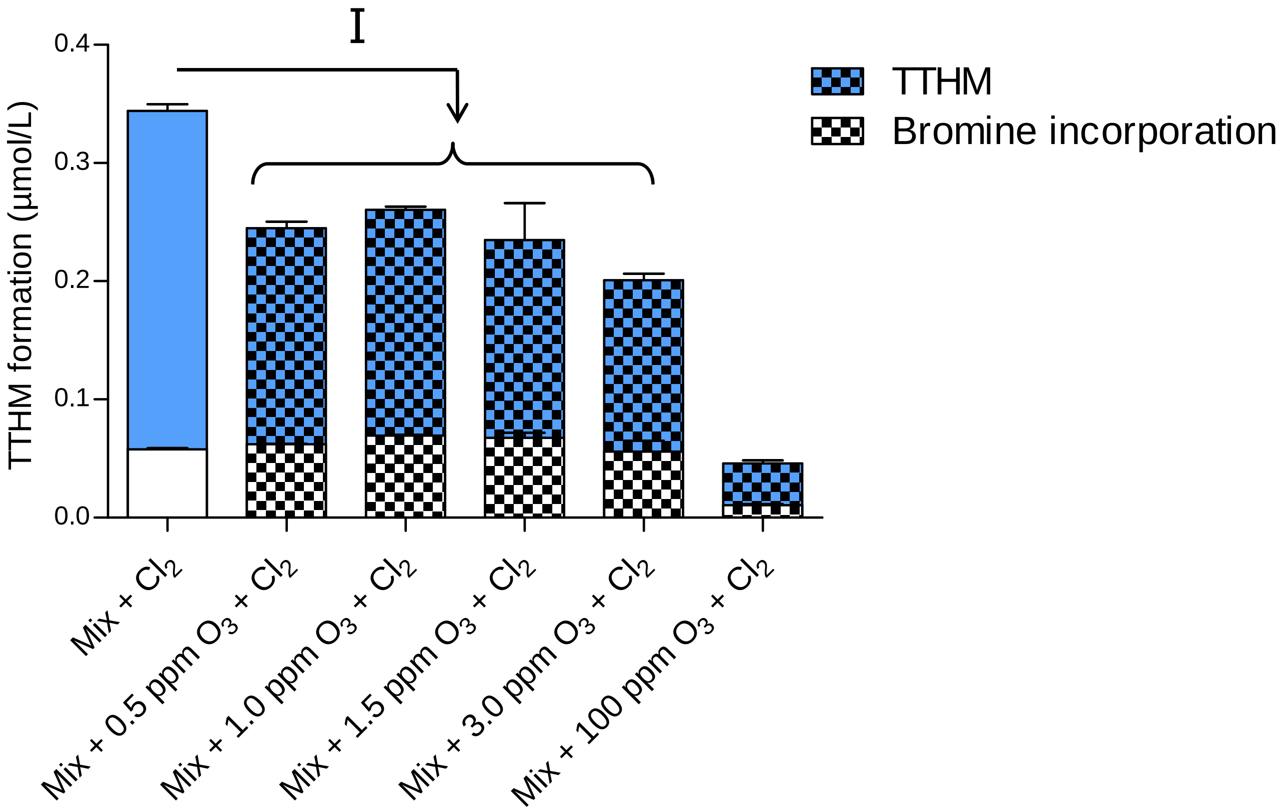
Total organic carbon (TOC) and chlorine consumption





- Ozonation decrease TOC
  and decreased chlorine consumption

TTHM formation



- Fresh pollutant direct ozone reaction → short ozone life time → no decrease in formation of brominated THM

Conclusions

Kinetic possible

- pH minimal effect
- TOC (ozone reactive vs non-reactive)

Chlorinated pool water

- Reaction via hydroxyl radical, making the organic material more reactive and increased THM formation.

Presence of fresh pollutants

- Direct oxidation by ozone → decreased THM formation

- Still need some more information on ozone dose required

Thanks for your attention

See you at the next pool conference with results from ozonation of full scale system